Materials Letters 66 (2012) 222–224

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Facile synthesis of fluorescent carbon dots using watermelon peel as a carbon source

Jiaojiao Zhou [a,1], Zonghai Sheng [a,1], Heyou Han [a,*], Mingqiang Zou [b,*], Chenxu Li [a]

[a] State Key Laboratory of Agricultural Microbiology, College of Science, Huazhong Agricultural University, Wuhan, 430070, PR China
[b] Chinese Academy of Inspection and Quarantine, Beijing, 100025, PR China

ARTICLE INFO

Article history:
Received 11 May 2011
Accepted 22 August 2011
Available online 27 August 2011

Keywords:
Carbon materials
Nanoparticles
Luminescence
Synthesis
Watermelon peel

ABSTRACT

The synthesis of water-soluble fluorescent carbon dots (C-dots) has received much attention recently. Here, high quality fluorescent C-dots have been synthesized through low-temperature carbonization and simple filtration using watermelon peel, a waste and reproducible raw resource, as a novel carbon resource. This facile approach allows large-scale production of aqueous C-dots dispersions without any post-treatment process. The as-prepared C-dots possess small particle sizes (~2.0 nm), strong blue luminescence, acceptable fluorescence lifetime and good stability in a wide range of pH values (pH 2.0–11.0) and at a high salt concentration. Besides, the obtained C-dots have been successfully applied in live cell imaging, indicating these carbon nanoparticles can serve as high-performance optical imaging probes.

1. Introduction

Fluorescent carbon dots (C-dots) are a class of recently discovered fluorescence nanomaterials [1]. Due to their small particle size (<10 nm), excitation wavelength dependent photoluminescence (PL) behavior and excellent biocompatibility, C-dots are attracting considerable attention as benign substitutes of quantum dots (QDs) for applications in bioimaging, biosensing and disease detection [2]. At present, a variety of methods have been developed to prepare fluorescent C-dots, including arc-discharge [3], laser ablation [4,5], electrochemical oxidation [6,7], combustion/thermal [8,9], supported synthesis [10] and microwave heating [11]. However, these approaches usually involve complex or post-treatment processes, or require expensive raw materials and severe synthetic conditions, which are unlikely to be extended significantly in the near future. Particularly, a lack of an efficient approach to producing processable fluorescent C-dots in large quantities has been a major obstacle to exploiting most proposed applications.

Here, we report that high-quality fluorescent C-dots can be readily obtained from watermelon peel, a waste and reproducible raw resource, through low-temperature carbonization and filtration. The ease of synthesis and the exceptional solution-phase processability of C-dots make this inexpensive and fluorescent nanostructure attractive not only for future nanobiosensors but also for large-scale applications in high-performance imaging. The obtained C-dots exhibit good water-solubility, small particle size (~2.0 nm), high luminescent efficiency and have been successfully applied in live cell imaging.

2. Experimental

2.1. Synthesis of fluorescent C-dots

The synthetic process of fluorescent C-dots mainly involves two steps (Scheme 1): (i) low-temperature carbonization of watermelon peel; and (ii) separation of the product by filtration. Typically, the fresh watermelon peel was firstly carbonized at 220 °C for 2 h under air atmosphere. The obtained product was dispersed in ultrapure water and sonicated for 30 min, and then filtrated with 0.2 μm filter membrane. The filtrate was centrifuged (18,000 ×*g*, 20 min), and the resultant supernate containing luminescent C-dots was dialyzed against deionized water for 48 h.

2.2. Materials characterizations

Fluorescence decay curves and PL spectra were obtained by a FLS 920 luminescence spectrometer. Raman spectra were recorded by a Renishaw inVia Raman spectrometer equipped with a He–Ne laser excitation source operating at 633 nm. HRTEM images were acquired by using a JEM-2010FEF transmission electron microscope operating at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was measured by a Thermo VG Multilab 2000 spectrometer. Cell imaging was performed on confocal laser scanning microscopy (LSM510 META).

3. Results and discussion

The C-dots were readily obtained from watermelon peel through low-temperature pyrolysis and filtration. The luminescent properties of C-dots were investigated. Fig. 1a shows the typical absorption and

* Corresponding authors. Tel./fax: +86 27 87288246.
E-mail addresses: hyhan@mail.hzau.edu.cn (H. Han), mingqiangz@sina.com (M. Zou).
[1] Equal contribution by the first two authors.

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.08.081

Scheme 1. Schematic illustration of the synthesis of water-soluble fluorescent C-dots from watermelon peel.

PL spectra of the C-dots. No obvious absorption peak but a wide absorption band is observed in absorption spectrum, which is possibly due to the relatively broad size distribution of C-dots [5,6]. The emission band maximum shifts to longer wavelengths (from 490 to 580 nm) with the increase of excitation wavelength. This excitation dependent feature is similar to those previously reported C-dots which may be attribute to the distribution of different emissive sites on each C-dots and different particle sizes of the C-dots [12,13]. The luminescent lifetime of C-dots was also measured, where a value of 5.72 ± 0.05 ns was obtained (Fig. 1b). Such a short lifetime is similar to that of QDs, and reveals the radiative recombination nature of excitations. The fluorescence quantum yield measured against an aqueous solution of quinine sulfate in 0.1 mol L^{-1} H_2SO_4 ($\lambda_{ex} = 340$ nm) is about 7.1%. The Scheme 1 presents the pictures of as-prepared C-dots observed under visible and ultraviolet light, respectively. Under visible light, the obtained C-dots solution is a light-yellow clear liquid, showing excellent water solubility. Under the radiation with 365 nm ultraviolet light, the as-prepared C-dots give off strong blue luminescence without any further treatments, such as chemical oxidation and surface passivation processes.

The obtained fluorescent C-dots exhibit fairly high monodispersity, and a uniform spherical morphology with a diameter of 2.0 ± 0.5 nm (Fig. 2a), which are amorphous demonstrated by the higher magnification image (see inset). As shown in Fig. 2b, Raman spectrum of the C-dots exhibit two broad peaks at around 1347.3 and 1583.4 cm^{-1}, attributing to the D-band (sp^3 hybridization) and G-

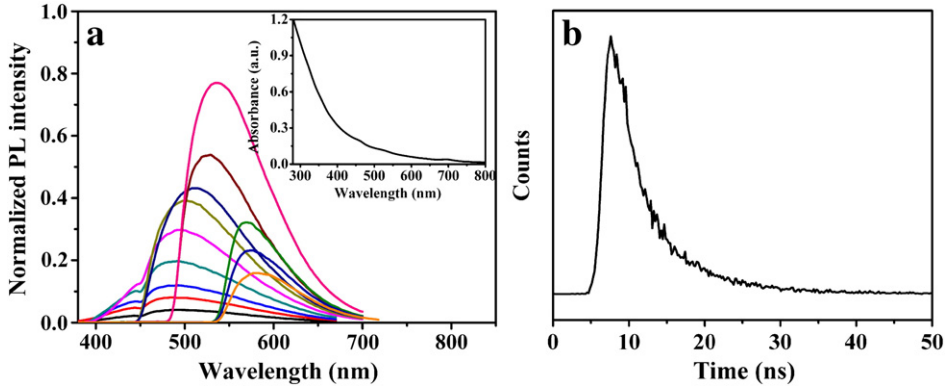

Fig. 1. (a) PL emission spectra (with progressively longer excitation wavelengths from 310 nm in 20 nm increment) and (b) Fluorescence decay curves of C-dots.

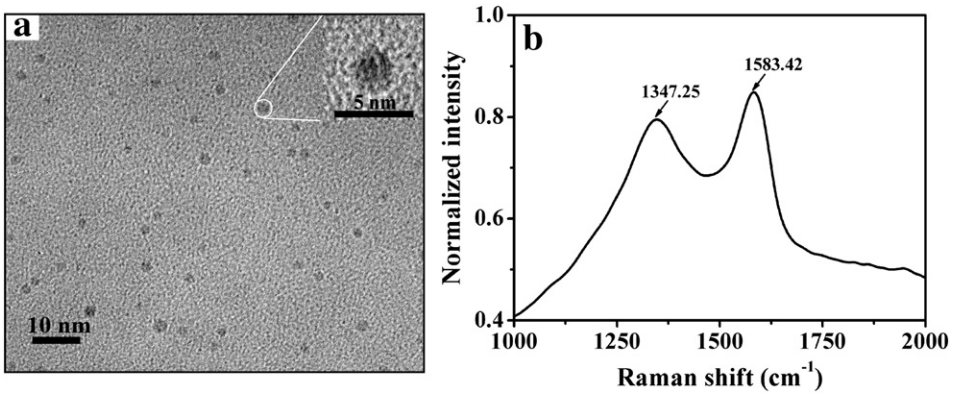

Fig. 2. (a) HRTEM image and the higher magnification image (inset). (b) Raman spectrum of C-dots.

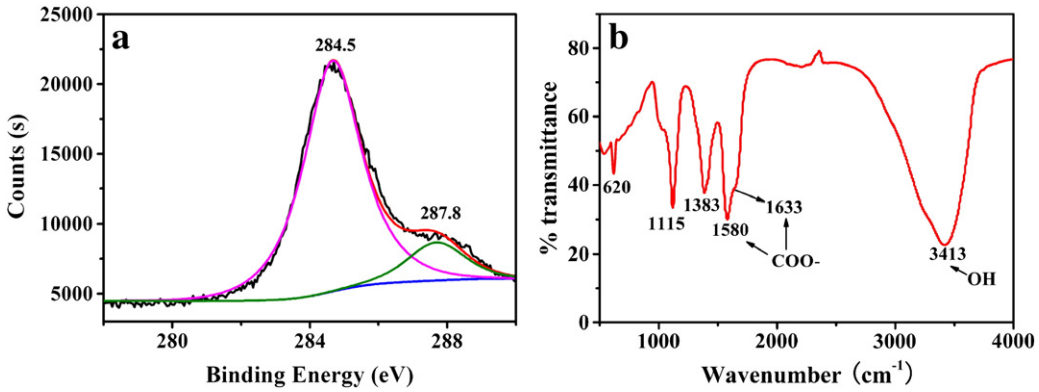

Fig. 3. (a) XPS and (b) FTIR spectrum of C-dots.

band (sp^2 hybridization), respectively. The coexistence of both bands indicates that the C-dots are amorphous [10], which is consistent with the HRTEM analysis. Elemental analysis reveals that the composition is C 64.65 wt.%, H 7.67 wt.%, N 1.13 wt.%, and O (calculated) 26.55 wt.%. The high carbon and oxygen content suggest that the obtained particles are probably nanoscaled carbonaceous material with a large number of carboxyl groups on the surface. The XPS results of C-dots exhibit two main peaks of C atoms at 284.5 (C–C, sp^3 hybridization) and 287.8 eV (C=O, sp^2 hybridization), respectively (Fig. 3a) and have confirmed that a large number of hydrophilic groups on the surface of the C-dots, resulting in the good water-solubility. As shown in FTIR spectra (Fig. 3b), the absorption peaks at 1580 and 1633 cm^{-1} are ascribed to C=O bond stretching, indicating the existence of carboxyl groups [9].

The solubility and stability of C-dots were also investigated. At room temperature, the C-dots display favorable solubility in different solvents (40 mg mL^{-1} in water, 16 mg mL^{-1} in methanol, 25 mg mL^{-1} in dimethyl formamide and 32 mg mL^{-1} in dimethyl sulfoxide). Furthermore, the C-dots reveal good stability in a wide range of pH values (pH 2.0–11.0) and at a high salt concentration (0.02 mol L^{-1} NaCl).

Due to small particle size, good water-solubility, high luminescence efficiency, the C-dots have been used as an ideal fluorescent probe for cell imaging. Fig. 4 shows confocal microscopy images of Hela cells incubated with C-dots for 3 h at 37 °C. Under the 488 nm excitation [10], bright luminescence of C-dots in the cell cytoplasm region was observed by using a laser scanning confocal microcopy. The results indicate that the C-dots have very good biocompatibility as bioimaging agents, and could be used as an excellent optical imaging probes.

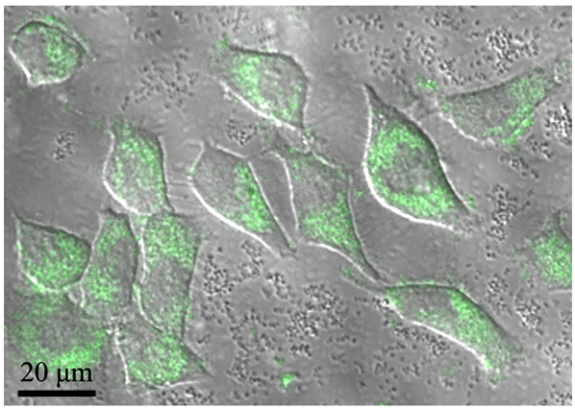

Fig. 4. Confocal microscopy image of Hela cell incubated with C-dots. (λ_{ex} = 488 nm).

4. Conclusion

In summary, this method offers several advantages over current synthetic techniques. Firstly, the process is facile without any complex or post-treatment procedures. Secondly, the starting material is green, economical and eco-friendly. Thirdly, the as-prepared C-dots possess good water-solubility, strong blue luminescence and acceptable fluorescence lifetime, and can serve as high-performance optical imaging probes. Particularly, this synthetic method is of great potential for large-scale synthesis of water-soluble C-dots.

Acknowledgments

The authors gratefully acknowledge the support for this research by National Natural Science Foundation of China (20975042), the Program for Academic Pacesetter of Wuhan (200851430484), International Science and Technology Cooperation and Exchange Foundation (2008DFA40270), the Fundamental Research Funds for the Central Universities of China (2010 PY 009, 2009JC005) and Genetically Modified Major Projects (2009ZX08012-015B).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matlet.2011.08.081.

References

[1] Jagadeesan D, Eswaramoorthy M. Chem Asian J 2010;5:232–43.
[2] Baker SN, Baker GA. Angew Chem Int Ed Engl 2010;49:6726–44.
[3] Xu XY, Ray R, Gu YL, Ploehn HJ, Gearheart L, Raker K, et al. J Am Chem Soc 2004;126:12736–7.
[4] Cao L, Wang X, Meziani MJ, Lu FS, Wang HF, Luo PJG, et al. J Am Chem Soc 2007;129:11318–9.
[5] Sun YP, Zhou B, Lin Y, Wang W, Fernando KAS, Pathak P, et al. J Am Chem Soc 2006;128:7756–7.
[6] Zhou JG, Booker C, Li RY, Zhou XT, Sham TK, Sun XL, et al. J Am Chem Soc 2007;129:744–5.
[7] Zheng LY, Chi YW, Dong YQ, Lin JP, Wang BB. J Am Chem Soc 2009;131:4564–5.
[8] Liu HP, Ye T, Mao CD. Angew Chem Int Ed Engl 2007;46:6473–5.
[9] Ray SC, Saha A, Jana NR, Sarkar R. J Phys Chem C 2009;113:18546–51.
[10] Liu RL, Wu DQ, Liu SH, Koynov K, Knoll W, Li Q. Angew Chem 2009;121:4668–71.
[11] Zhu H, Wang XL, Li YL, Wang ZJ, Yang F, Yang XR. Chem Commun 2009;34:5118–20.
[12] Bourlinos AB, Stassinopoulos A, Anglos D, Zboril R, Georgakilas V, Giannelis EP. Chem Mater 2008;20:4539–41.
[13] Li XY, Wang HQ, Shimizu Y, Pyatenko A, Kawaguchi K, Koshizaki N. Chem Commun 2011;47:932–4.